



PATENT SPECIFICATION

600,451

Convention Date (United States of America): Nov. 6, 1940.

Application Date (In United Kingdom): Sept. 20, 1941. No. 12181/41.

Complete Specification Accepted: April 9, 1948.

EXAMINER'S
COPY

Index at acceptance:—Classes 15(ii), B2c(1a5: 2c: 2d1b: 2h), B2m; and 146(iii), C3. DIV.-----

COMPLETE SPECIFICATION

Direct Dye Planographic Printing Compositions

We, AMERICAN CYANAMID COMPANY, a corporation organized under the laws of the State of Maine, United States of America, and having its principle place of business at 30, Rockefeller Plaza, New York, New York, United States of America, (Assignees of CHESTER ALBERT AMICK, residing at 121, East Maple Avenue, Bound Brook, New Jersey, United States of America, a citizen of the United States of America), do hereby declare the nature of this invention and in what manner the same is to be performed, to be particularly described and ascertained in and by the following statement:—

This invention relates to putty compositions for planographic printing on cellulosic material employing direct dyes which are capable of being directly affixed to such cellulosic materials.

In the past the printing of cellulosic materials has been accomplished almost exclusively by use of the intaglio method. In this method a relatively free flowing printing paste containing the colour to be printed is applied to an engraved printing roll, usually copper, for example by means of a furnisher roller, the excess paste scraped off the roller so that paste remains only in the depressions, and the roller applied to the fabric in a printing machine. This procedure, while satisfactory for many types of designs, has a number of disadvantages. In the first place, it is not possible to produce designs with extremely fine, close fitting, interwoven, multicoloured lines without a certain amount of running or smudging of the lines, because it is necessary to have a rather free flowing printing paste or otherwise it will not print satisfactorily. Multicolour printing is also a very serious problem because each colour requires a separate roll and a sharp print requires accurate alignment and synchronism of the different printing rolls. When a great number of colours are to

be printed a further disadvantage is the large amount of capital which has to be tied up in engraved rollers.

Planographic printing, in which the surface is contacted with a solid putty or block of colour and a portion of the colour is transferred to form a print, presents many advantages. This method of printing has not been applied to cellulosic fabrics. When direct dyes are printed onto cellulosic materials by means of the intaglio method, it is customary to incorporate in the printing paste a thickener to produce the desired viscosity, a carbohydrate gum and the direct dye, with a fixing agent, for example urea, as well as a material such as glycerine to maintain the desired degree of wetness of the paste. If it is attempted to produce a composition of the viscosity required for planographic printing by changing the amount of water and viscosity of the paste for intaglio printing, a putty can be produced, but while it is possible to print planographically on cellulose material from such a putty immediately after it has been formed, it rapidly disintegrates on exposure to humid atmosphere, a condition which is practically impossible to prevent in commercial printing plants, and hence such a printing putty cannot be used practically.

According to the present invention we have found that putties containing direct dyes can be prepared which are practically printed on cellulosic material under ordinary conditions and which will not deteriorate almost immediately on exposure to moist atmosphere. The present invention is based on several features, one of which appears to be essential for practical results, and others are desirable for producing the best results.

The most important single feature is the elimination of the hygroscopic agents such as glycerine or other hygroscopic

alcohols while retaining urea as fixing agent in the putty. The present invention is not intended to be limited to any particular theory of action but we believe that the avoidance of the combined presence of hygroscopic agents such as glycerine and such fixing agent is one of the main factors. Fixing agents such as urea often exert marked hydroscopic properties and as a result moisture picked up by the hygroscopic alcohol which might otherwise not be a serious factor, will result in large viscosity changes in the presence of the fixing agent. The printing putty is a complex mixture and it is possible that there are other factors which are of equal or greater importance and the above explanation is advanced merely as one which appears probable from the present state of knowledge of the process.

For best results we find that other features are desirable although not essential to obtaining prints. One of these features is the incorporation in the putty of a waxy material such as glyceryl mono-ester of a higher fatty acid. These agents appear to act in controlling the plasticity of the putty, aiding in giving it a long softening range and also appear to effect better transfer of the coloured putty in planographic printing.

A further feature which is of advantage in obtaining the best results is the incorporation in the putty if a soap such as a low tire olive oil soap. This appears to give in part improved sharpness and strength to the prints. It is, however, not as important in obtaining best results as is the incorporation of a waxy material.

Another important feature which is part of the preferred modification of the present invention is the use of a rather more completely dextrinized material. It has been common practice in textile printing to use either a natural gum or a rather heavy bodied, not extensively dextrinized carbohydrate such as white dextrin of the British gum type. It would ordinarily be expected that these materials would give better bodied putties. We have found, however, that the contrary is the case when dealing with putties containing direct dyes suitable for planographic printing; the best putties being obtained when highly dextrinized materials such as yellow corn dextrin are used. This constitutes a feature of the preferred embodiment of the present invention and is of importance where results of the highest quality are required although entirely satisfactory prints can be obtained with less highly dextrinized materials.

It is also desirable to incorporate in the putties a small amount of a wetting agent for which esters of sulpho-succinic acid have proven to be very useful and also a small amount of trisodium phosphate appears to improve the consistency of the putties.

Another ingredient which may be added and which is useful in producing the best results is bentonite, preferably in a somewhat hydrated or gelatinous form, and this is a further feature of the preferred embodiment of the invention.

Putties free from hygroscopic substances, but containing a carbohydrate gum and an amide having the group $C(NH_2)_2$, are thermoplastic and have a long plastic range. They are sufficiently hard at atmospheric temperatures to resist deformation during printing, but not so hard as to be brittle or unable to flow under pressure. They soften on heating, and regain substantially their original hardness on cooling again to atmospheric temperatures, and can be softened by heat and hardened again on cooling repeatedly, without setting permanently or losing the power to soften when heated. They have a long softening range, remaining plastic over a range at least of the order of $100^{\circ} F.$ so that they neither break or crumble at lower temperatures nor spread or smear at higher temperatures within this range.

The range of hardness exhibited may be expressed by means of a penetrometer, for example the instrument described in the 1942 Edition of the American Society of Testing Material Standards, D 517—40, Paragraph 17. The indentation with 500 gms. load should be not less than about 0.6 cm. at $37^{\circ} F.$ in ten minutes, and not more than about 2 cm. at $80^{\circ} - 85^{\circ} F.$ in six minutes.

The reference to cellulosic material in the present invention is not intended to be limited to natural cellulose fibres themselves. On the contrary, it includes not only natural cellulose fibres such as cotton, linen and the like, but also regenerated cellulose such as viscose and other regenerated cellulosic rayons, and the like.

The invention will be described in conjunction with the following specific examples, but it is not limited to the details therein set forth. The parts are by weight.

EXAMPLE 1.

120 parts of Calcomine Fast Scarlet 4BSY (C.I. 326) were pasted with 100 parts of mono ethyl ether of ethylene glycol and 600 parts of water. To this were added 480 parts of urea whereupon the colour appeared to go into solution. This

colour solution was then cold pasted with 1000 parts of yellow dextrine in a dough mixer until uniform. The steam valve was slightly open, the dextrin cooked at 5 a temperature of 165° F. or slightly above for 15 minutes. 200 parts olive oil soap, 40 parts glyceryl mono stearate, 10 parts trisodium phosphate and 10 parts of isobutyl ester of sodium sulpho succinic acid were added after having been previously pasted with 100 parts of boiling water in a separate container. Evaporation of moisture from the dough mixer was continued under vacuum until a thin 10 section, chilled by cooling on an ice cold tin, fractured when bent by hand or struck a blow with a blunt instrument. When printed by the planographic method this colour transferred uniformly, giving a bright smooth blue print.

EXAMPLE 4.

750 parts of the product prepared in the preceding example and 150 parts of a 7% bentonite gel containing 1% sodium carbonate were worked in a small dough 30 mixer to which heat was applied externally from a Buusen burner. The water was evaporated until the same test was obtained as in Example 1. This product gave good smooth prints when applied planographically to cotton. The addition of the bentonite reduced the tackiness of the solid product as compared to that obtained in Example 1.

EXAMPLE 3.

40 120 parts of Direct Sky Blue FF (C.I. 518) were pasted with 100 parts of monoethyl ether of ethylene glycol and 600 parts of water. To this were added 480 parts of urea whereupon the colour 45 appeared to go into solution. This colour solution was then cold pasted with 1000 parts of yellow dextrin in a dough mixer until uniform. The steam valve was slightly open, the dextrin cooked at 50 a temperature of 160° F. or slightly above for 15 minutes. 200 parts of olive oil soap, 40 parts glyceryl mono stearate, 10 parts trisodium phosphate, and 10 parts of isobutyl ester of sodium

sulphosuccinic acid were added after having been previously pasted with 100 parts of boiling water in a separate container. Evaporation of moisture from the dough mixer was continued under vacuum until a thin section, chilled by cooling on an ice cold tin, fractured when bent by hand or struck a blow with a blunt instrument. When printed by the planographic method this colour transferred uniformly, giving a bright smooth blue print.

EXAMPLE 4.

Pieces of the products of Examples 1, 2, and 3 were formed into a composite printing block in the form of a design in the different colours. When printed by 70 planographic methods on pigmented rayon a sharp print of the design in the different colours was obtained. No tendency toward running of the edges of the different colours in the designs are noted.

Having now particularly described and ascertained the nature of our said invention and in what manner the same is to be performed, we declare that what we claim is:—

1. A putty suitable for planographic printing comprising a direct colour capable of being fixed on cellulose, urea and a carbohydrate gum, the product being substantially free from hygroscopic 85 alcohols, and showing good keeping qualities when exposed to ordinary moist atmosphere.

2. A putty according to Claim 1 which contains yellow corn dextrine.

3. A putty according to Claims 1 and 2 which contains a soap.

4. A putty according to Claims 1 to 3 which contains a waxy material.

5. A putty according to Claims 1 to 4 95 which contains a glyceryl mono ester of a higher fatty acid.

6. A putty according to Claims 1 to 5 which contains bentonite.

7. A putty according to Claims 1 to 6 100 which contains a wetting agent.

Dated this 20th day of September, 1941.

CRUIKSHANK & FAIRWEATHER,

29, Southampton Buildings,

Chancery Lane, London, W.C.2, and

29, St. Vincent Place, Glasgow,

Agents for the Applicants.